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Effect of Solvent on Semiconductor Surface Electronic States:

A First-Principles Study

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Abstract

In this paper the first step is taken toward a first-principles molecular theory of the liquid-semiconductor interface. The focus is on the degree of rigor that must be applied to the solvent in order to obtain a realistic description of the interfacial electronic properties. To accomplish this, two different water solvent geometries on the H/Si(111)1×1 surface are assumed, and the electronic structure of the system is calculated using two different models for the water molecules, one which includes the electrons of water explicitly and one which does not. It is found that for a realistic description of the surface electronic structure it is necessary to use an *ab initio* description of the solvent molecules for at least the first layer due to the electronic state mixing. The issues of broken symmetry of the crystal surface and possible dissociation of the solvent molecules are also discussed.

I. INTRODUCTION

The hydrogen-terminated (111) surface of Si possesses electronic surface states in its valence band gaps which have been the subject of both experimental and theoretical investigations (see, e.g., Refs 1-8). Surface states are a key feature in determining the rate of

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electron transfer across an interface, particularly within the context of photoelectrochemical devices.⁹⁻¹¹ In this vein, the bare semiconductor surface is of less relevance than the interface with an aqueous solution, the latter being the more common environment for working electrodes, wet-etching processes, etc. To extend experimental and theoretical investigation into this regime, however, is highly nontrivial. For example, the photoemission techniques which provide information on the electronic surface states of bare surfaces are not useful for the interface, and the theoretical challenges of placing a disordered many-body solvent on the surface, especially for first-principles electronic structure calculations, are numerous.

Previous first-principles density functional studies of this solid surface have used a plane wave plus pseudopotential approach, in which only the valence electrons are included explicitly, and their orbitals are represented using a plane wave basis set. The inclusion of water solvent valence electrons in such an electronic structure calculation greatly increases the number of orbitals in the calculation. This is compounded by the fact that when a plane wave plus pseudopotential approach is used, the basis-set size depends on both the atomic species present and the size of the simulation cell. These effects increase the size of the solvated surface calculation relative to the bare surface one: the atomic species change by the inclusion of oxygen, which has a much steeper pseudopotential than hydrogen and silicon, and the size of the simulation cell must be increased to accommodate all of the solvent. Furthermore, there is a question whether the disordered solvent can break the crystal surface symmetry. A subset of the above difficulties will be addressed in the present paper within the context of the $\text{H}_2\text{O-H/Si(111)1}\times\text{1}$ interface. This system has assumed a particular importance since the work of Chabal and coworkers¹²⁻¹⁵ has made possible the synthesis of a very low defect $\text{H/Si(111)1}\times\text{1}$ surface.

In the present study, the aim is to learn the degree of rigor that must be employed to obtain a realistic picture of the semiconductor surface electronic states in the presence of water. Specifically, the goal is to determine whether the surface states maintain their integrity, or interact with the solvent, or vanish altogether. To do this, the surface will be studied using first-principles density functional techniques in the presence of either a

water monolayer or a bilayer. The geometry of the layers is chosen by the method described below in detail. Moreover, the various calculations will treat the water molecules with different degrees of rigor. In some calculations all of the valence electrons of water will be included explicitly. In others, the water will be represented by a simpler pseudopotential, which will not explicitly include any of its electrons. In one of the bilayer calculations, the innermost water layer will have explicit valence electrons while the upper layer will not. From this systematic study, much can be learned about the strength of the solvent's electronic interactions with the surface, as well as the range of these interactions.

The present paper is organized as follows: In Sec. II, the details of the first-principles calculations will be outlined. Then, the results will be presented in Sec. III and discussed in Sec. IV.

II. DETAILS OF THE FIRST-PRINCIPLES CALCULATION

A. Cell geometry and ion configurations

In the system studied in this paper, the silicon crystal and its surface were represented by a ten-layer slab of silicon. The surface was in the (111) plane and the dangling bonds perpendicular to the surface were terminated by hydrogen atoms. The layers of the slab were relaxed to bare surface geometries as given in Table I. The slab extended infinitely in the directions parallel to the surface and was periodically replicated in the z -direction perpendicular to the surface. Hydrogen nuclei at the bottom of one slab and at the top of the slab just below it were separated by ~ 21 a.u. Specifically, the supercell edges were 14.51154 a.u. parallel to the slab and 52.00000 a.u. perpendicular to the slab. The crystal axes parallel to the slab formed an angle of 120° (see, for instance, Figure 3). In previous calculations³⁻⁷ the region between the slabs was vacuum, but in this study it contained molecules of water organized into layers.

Various experimental studies have indicated that atomically smooth H/Si(111)1×1 is hydrophobic,¹⁶⁻¹⁹ and that etching of the surface by hydroxyl ions occurs primarily at step edges. Accordingly, the molecularly intact water was placed in certain layer configurations. Annealing these layers tested, to a degree, the assumption of hydrophobicity. The specific configurations of the water molecules were not crucial in this study, but the relevant information for the bilayers is given for completeness in Table I. [The configurations of the first-layer waters are also illustrated later in Figure 3(a).] In this arrangement the first layer was comprised of both symmetric waters, which were roughly parallel to the surface, and asymmetric waters, which had one bond roughly parallel to the surface and one roughly perpendicular. The perpendicular bonds pointed up towards the symmetric and roughly planar waters of the second layer, while the asymmetric waters in the second layer had bonds pointing down towards the symmetric waters of the first layer.

The choice of water arrangement in the simulations was suggested from two sources, Refs 20 and 21. In Ref. 20 the results of an semi-empirical potential for water on H/Si(111)1×1 supports the notion that individual water molecules adsorb in a roughly planar manner with the hydrogen atoms slightly lower than the oxygen. We have also found this to be true from *ab initio* annealing studies. The water molecules were also shown to be located in the spaces between the capping hydrogens. In Ref. 21, the adsorption of water on the (111) surface of some fcc metals showed a tendency to form hexagonal rings. The water-water distances parallel to the plane are artificially small in the present system in order to be commensurate with the lattice, but the interlayer distances are similar to those in ice and water. Since it is the orbital interactions in the *z*-direction that are of key interest here, this seems a reasonable model for the present work. The positions generated from the parameters in Table I represent a partially annealed geometry to allow comparison of the electronic structures of the two water models. Further annealing was also performed with both models.

The surface supercell is composed of four primitive hexagonal surface cells in a 2×2 arrangement, which is equivalent to using a single primitive cell with four special *k*-points in

the surface Brillouin zone, namely, the Γ point and three M points, all with equal weights. This is convenient since one of the surface states is present at the M point. The k-point information relevant to the band structure can be extracted by diagonalizing the electronic orbitals in symmetry groups. This approach will be more relevant to the electrode-water interface than standard Brillouin zone sampling since a single unit cell is inappropriate in the presence of a solvent.

B. Computational method

The electronic structure calculation is performed using density functional theory (DFT) as formulated by Kohn and Sham.²² The exchange-correlation part of the density functional consists of the local density approximation (LDA) for the exchange and correlation (using the Perdew and Zunger²³ parametrization of quantum Monte Carlo results from Ceperly and Alder²⁴) and a gradient correction for the exchange given by Becke.²⁵ This combination was found to be efficacious in the *ab initio* study of liquid D₂O.²⁶ The DFT is implemented using the method of Car and Parrinello.²⁷

C. Pseudopotentials

The Car-Parrinello program was extensively modified to incorporate Vanderbilt pseudopotentials.²⁸ A Kleinman-Bylander representation²⁹ of a norm-conserving pseudopotential³⁰ was used for silicon, and Vanderbilt pseudopotentials were used for oxygen and hydrogen. The latter two are obtained by a procedure similar to that in Ref. 26 with the values $r_c = 1.3$ a.u. for oxygen and $r_c = 0.6$ a.u. for hydrogen. The energy cutoff is 25 Rydbergs. The water molecules represented by valence electrons and Vanderbilt pseudopotentials will be referred to as VV-water. For comparison with this *ion-core* pseudopotential approach, some of the calculations will feature water represented by a simpler *molecular*

pseudopotential. This describes the interaction of the whole neutral water molecule with the surface electron density outside the molecule. This molecular pseudopotential was devised by Schnitker and Rossky³¹ in connection with path integral simulations of electron solvation, and is a sum of separate local pseudopotentials for hydrogen and oxygen. We use a slightly modified version of the oxygen part of the pseudopotential. Instead of a positive divergence at $r = 0$, it is replaced within $r_c = 1$ a.u. by a polynomial function which matches the zeroth, first, and second derivatives at r_c and which at $r = 0$ has a value of 20 a.u. and a slope of zero. Since a negligible amount of electron density penetrates the center of the oxygen, this modification has no effect on the results, but allows the calculation to proceed more smoothly. The molecular pseudopotential is also a flexible model,³² since the O-H bond lengths and angles are adjusted to *ab initio* values for the surface waters for the comparison calculations, and are further adjusted in a separate annealing for this model. A molecule represented by this model will be referred to as SR-water. When only SR-water is present in a calculation, a cutoff energy of 12 Rydbergs is sufficient for energy convergence. These calculations are roughly an order of magnitude faster than those with VV-water, both because of the lower cutoff, as well as the significantly smaller number of electrons. The possibility of using SR-water with its significantly smaller computing requirements provides much of the motivation for this study.

D. Computational details

The calculations were performed on an IBM RISC/6000 Model 590 workstation. Each of the larger calculations required several days to run. As well as the usual energy convergence criterion, the progress of a run was monitored by observing the symmetry of the orbitals. Since the potential due to the ions was constructed to possess inversion symmetry, each (diagonalized) orbital should have had plane wave coefficients which were either purely real or purely imaginary. Orbitals pertaining to water were slower to converge to the proper

symmetry than those inside the slab.

III. RESULTS

A. Effect of a solvent bilayer

Four calculations were performed based on the parameters listed in Table I. First, for purposes of comparison, a bare H/Si(111)1×1 slab calculation was performed to obtain the electronic structure at the Γ and M points. The results were essentially identical to those reported previously^{3,4} and will be described later. Second, the slab was covered with two layers of SR-water. Third, the slab was covered with two layers of VV-water. Fourth, the layer of water next to the slab was composed of VV-water and the second layer was composed of SR-water, making an SR/VV-water calculation. After each calculation, the matrix $H_{ij} = \langle \phi_i | H_{KS} | \phi_j \rangle$ was calculated, where $\{\phi_i\}$ are the Kohn-Sham orbitals, and H_{KS} is the Kohn-Sham Hamiltonian. This matrix was diagonalized to obtain the eigenvalues and eigenorbitals, from which were selected those corresponding to the surface states. Although Kohn-Sham orbitals pertain rigorously only to a reference system of non-interacting electrons,²² experience has shown them to be good approximations to occupied one-electron orbitals of interacting electrons. For instance, very similar energies can be obtained using orbitals from both DFT and Hartree-Fock theory,^{25,33} and DFT orbitals are virtually identical to those obtained from a more sophisticated self-energy approach.³⁴ This is due to the dominance of kinetic energy over electrostatic interactions for high density fermions. Thus, in agreement with previous workers,³⁻⁷ we will use the eigenorbitals as representative of the physical surface states.

Information from the surface state eigenorbitals of the first three runs is given in Figures 1 - 3. In Figure 1 the quantity $\int |\phi_i(x, y, z)|^2 dx dy$ is plotted against z to show the extent to which the surface bands extend beyond the surface in the various models. This shows

immediately one of the key results, namely, that the pseudopotential-based SR-water result is very similar to that for the bare slab, but very different from that of the VV-water calculation. The nature of the extra peak in the first-principles VV-water is shown in greater detail in Figs 2 - 3. Figure 2 displays a contour plot for a slice of $|\phi_i(x, y, z)|^2$ for one of the surface states, where the slice is perpendicular to the slab and passes through the long diagonal of the hexagonal surface cell. This illustrates that the principle part of the density is still on the hydrogen nuclei ($z \sim 15$ a.u.) and in the outermost silicon layer ($z \sim 12$ a.u.), but a significant amount has spread into the first water layer ($z \sim 17$ a.u.). Figure 3(a) displays a contour plot for a slice of $\sum_i |\phi_i(x, y, z)|^2$ parallel to the slab and passing roughly through the first plane of waters. The summation is over all three symmetrical surface states, with the antisymmetrical states giving identical plots. The positions of the water molecules are also indicated. Figure 3(b) is similar to Figure 3(a) but is given for just one of the symmetrical surface states, namely, the state shown in Figure 2. The other two are related to it by 120° rotations. Such a set of three rotationally related orbitals is characteristic of M-point states in the surface Brillouin zone. These figures illustrate how the surface state electronic density populates the valence molecular orbitals of the water.

From the results displayed above, one conclusion is immediately clear. The two models of water do not yield the same picture of the water-semiconductor interface. The presence of the pseudopotential-based SR-water results in only a perturbation of the bare slab results, with surface states essentially maintaining their integrity, while the surface states couple non-negligibly with the electronic states of the first-principles VV-water. Although the water is in a rather idealized configuration, it is apparent that a correct description of semiconductor surface electronic structure in the presence of solvent will require explicit consideration of the valence electrons of the solvent.

Figures 1 - 3 also suggest that there is negligible coupling to the second layer of VV-water, so including only one layer of VV-water may be sufficient to give an accurate description in many systems. In Figure 4 the z -dependence of the electron density is compared for the VV-water and SR/VV-water calculations, and the similarity of these plots is further

evidence that interactions are essentially limited to the first layer.

We believe these results regarding the existence and range of surface-solvent interactions will prove to be very significant for interfacial electron transfer reactions. This process depends critically on the overlap of the surface electron density with the redox ion orbital.^{35,36}

The eigenvalues of the surface states (referenced to the highest eigenvalue of the slab valence band) are shown in Table II. There is splitting observed between symmetric and antisymmetric orbitals because of the finite width and separation of the slabs. More accurate surface state energies can be calculated by self-energy techniques³ but these are very demanding calculations which cannot yet be applied to a solvent-electrode interface. Table II shows important trends though, namely, that the eigenvalues for an SR-water bilayer are decreased relative to the bare surface, while the VV-water and SR/VV bilayers have increased eigenvalues. These last two numbers are also in relatively good agreement with each other. Furthermore, the increased lack of agreement between the three symmetry related M-point values of the VV- and SR/VV-calculations shows that the full hexagonal symmetry of the surface states is significantly broken by the VV-water, but not by the SR-water. These observations confirm further the necessity of using an electronically explicit model of water in the first solvent layer.

Further annealing of the VV-water layers resulted in the first layer drawing slightly closer to the surface. If anything, this would enhance the mixing, but in general the results were similar to those displayed. No evidence of molecular dissociation was detected, although the idealized geometry used in the study cannot be considered a rigorous probe of this phenomenon. Further annealing of the SR-waters resulted in a slightly different geometry with the symmetric waters of the first layer moving slightly inward and the asymmetric waters moving slightly outward. It is impossible to say at present whether this apparent difference between the models would have any substantial effect on surface structural properties, such as surface phonons. Eventually the annealing of both models resulted in a breaking up of the metastable layer configuration. This breakup presumably leads into a semi-ordered interfacial configuration. Its structural properties would be of considerable interest, but are

beyond the scope of this study.

B. Effect of an uncomfortable monolayer

Another perspective on solvent effects is given by two runs in which the second layer of water was removed and only one layer of either SR- or VV-water remained. The configuration was similar to that given in Table I except for the important difference that half of the waters were placed in energetically unfavorable sites directly over the capping hydrogens. Such a calculation can be motivated by the fact that, in a realistic solvent, fluctuations will occasionally place molecules in high-energy sites. Some results of these calculations are shown below.

In the case of pseudopotential-based SR-water the surface states are strongly modified, with electron density pushed further into the slab (Figure 5). The VV-water model, though, exhibits an opposite effect from the SR-water model, drawing surface electron density into the water valence orbitals. In addition, one of the surface states (not shown) for the VV-water case mixes strongly with the inner slab states, showing the possibility of further complex behavior.

At the same time, one of the upper valence bands is also observed to be strongly modified. For the SR-water calculation this means that electron density actually is moved out into the ~ 12 a.u. void between the water layers on adjacent slabs [Figure 6(a)]. We note that since four of the sixteen protons of each layer are projecting into this region, it is likely to be rather electropositive. However this same effect was *not* seen if the one layer of water was arranged as suggested in Table I, which should have the same electropositive zone. Thus it is the proximity of oxygen to the capping hydrogen which is primarily responsible for this effect. This is consistent with the rather different results obtained when first-principles VV-waters were used. In this case the above-mentioned valence band mixes strongly with orbitals of the water molecules, but does not move beyond them into the vacuum region

[Figure 6(b)]. Thus it appears that the solvent may be able to form surface resonances out of bulk states, but in ways which depend sensitively on the nature of the solvent model.

Finally, the eigenvalues of the surface bands are shown in Table III, and they display trends different from those observed in Table II. Now both the SR-water and VV-water raise the eigenvalues relative to the bare surface, and the SR-water eigenvalues are now higher than those of the VV-water. This suggests that a larger energy scale is involved in populating the vacuum region between SR-waters than in mixing with the valence orbitals of VV-waters.

IV. DISCUSSION

The interesting coupling of the surface electronic states to the solvent configurations should be quite significant for electron transfer reactions across interfaces. This effect has not yet been included in even the most detailed model of such processes.³⁵ There are at least two ways that a proper *ab initio* model of water changes the surface electronic states of H/Si(111)1×1. At low-energy configurations, the surface state density is perturbed by a spreading into the molecular orbitals of water molecules. At more intense interactions the surface states are significantly altered, and the electron density higher in the valence band moves out of the surface as well. In neither case is the effect represented correctly by a molecular water pseudopotential in which electronic states are not treated explicitly. At the same time, the studies performed with two layers suggest that interaction effects do not extend to the second layer. Furthermore, the electronic interaction does not appear in this case to readily result in dissociative adsorption, but if there were the possibility of chemical association, the inclusion of a layer of *ab initio* water molecules would be even more important in the simulation. Such a possibility has been raised in H/Si(111)1×1 atomic force microscopy studies.³⁷

The implications of the present study for the large-scale simulation of a solvent-

semiconductor interface are that a molecular pseudopotential for water is sufficient for most of the water molecules, with the exception being for those waters closest to the surface which should be treated from first principles with ion-core pseudopotentials. Such implications presumably hold for other solvent-semiconductor systems and possibly more general systems as well. For instance, although electron solvation has been studied often using molecular pseudopotentials for the solvent (see, e.g. Ref. 32), a layer of *ab initio* solvent may be crucial for some properties. Also of considerable interest is the solvent-metal interface, for which solvent effects may be of even more importance than the hydrophobic semiconductor surface studied here. Price and Halley³⁸ have recently studied a simplified model of the water-electrode interface using a molecular dynamics method. They note that their model is not directly related to any physical system because of the crude metal pseudopotential employed. The present study suggests that their method, which used a water model similar to the Schnitker-Rossky potential, must also be upgraded to include at least some *ab initio* waters.

Finally, even though the symmetry of the crystal surface is broken, it was clear in the present study, and will probably be true for a disordered solvent as well, that states are present which can clearly be identified with various k-points of the bare surface. Thus, one should be able to extract information from the supercell which is relevant to solvent-averaged band structure calculations, such as that shown in Tables II and III. In future publications, the methods outlined in this paper will be extended to other systems and the results implemented in theoretical formulations of interfacial electron transfer processes.^{9,35,36}

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TABLES

TABLE I. Numerical quantities defining the geometry of the water-slab system.

Quantity	Value (a.u.)
Si ² -Si ³ ^a	4.454
Si ¹ -Si ² ^b	1.435
H ^c -Si ³ ^c	2.92
O ^{1S} -H ^c ^d	1.76
O ^{1A} -O ^{1S} ^e	0.13
O ² -O ¹ ^f	5.22
OH ^A (x, y, z) ^g	(1.689 , 0.970 , 0.4302)
OH ^{B1} (x, y, z) ^h	(0.0 , 2.23 , 0.34)
OH ^{B2} (x, y, z) ⁱ	(0.0 , 0.25 , 1.897)

^adistance in z -direction between second and third layers of silicon.

^bdistance in z -direction between first and second layers of silicon.

^cbondlength between capping hydrogen and outermost silicon layer.

^ddistance in z -direction between layer of capping hydrogens and oxygens of symmetric waters in first layer.

^edistance in z -direction between oxygens of asymmetric and symmetric waters in each water layer.

^fdistance in z -direction between oxygen of asymmetric water in first water layer and of symmetric water in second water layer.

^gdistance in x, y, z -directions between hydrogen and oxygen of a symmetric water.

^hdistance in x, y, z -directions between oxygen and \parallel -hydrogen of asymmetric water.

ⁱdistance in x, y, z -directions between oxygen and \perp -hydrogen of asymmetric water.

TABLE II. Band structure points calculated at the M-point surface states for the bare surface and for bilayer calculations. The spread of values in the last digit is indicated by the number in parentheses. Energies are given in electron-volts and are taken relative to the top of the valence band of the slab.

Calculation	symmetric	asymmetric
bare surface	-3.857(1)	-3.709(1)
SR-water layers	-3.951(1)	-3.818(1)
mixed SR/VV layers	-3.74(3)	-3.62(3)
VV-water layers	-3.69(3)	-3.55(3)

TABLE III. Band structure points calculated at the M-point surface states for the bare surface and for monolayer calculations. The spread of values in the last digit is indicated by the number in parentheses. Energies are given in electron-volts and are taken relative to the top of the valence band of the slab.

Calculation	symmetric	asymmetric
bare surface	-3.857(1)	-3.709(1)
SR-water layer	-3.406(1)	-3.315(1)
VV-water layer	-3.67(8)	-3.4(2)

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FIGURES

FIG. 1. Effect of two layers of water on the z -dependent density of the asymmetric M-point surface states of $\text{H}/\text{Si}(111)1\times 1$. The solid curve refers to the bare surface result, the dot-dashed curve to two layers of SR-water, and the dashed curve to two layers of VV-water. Positions of the planes of silicon, capping hydrogen, and water oxygens are indicated by labeled vertical lines beneath the axis.

FIG. 2. Contour plot of electron density of an M-point surface state in the VV-water bilayer calculation. The plot is perpendicular to the surface along the long diagonal of the surface cell.

FIG. 3. (a) Contour plot of the combined electron density of the three symmetric M-point surface states in the VV-water bilayer calculation taken parallel to the surface at a z -value close to that of the first water layer. The positions of capping hydrogens are indicated by the letter H, and the water molecules of the first layer by combinations of lines and triangles. The in-plane O-H bonds are indicated by a line, and out-of-plane water bonds are indicated by a triangle. (b) Contour plot of electron density of one single symmetric M-point surface state in the VV-water bilayer calculation taken at the same coordinates as part (a) of this figure.

FIG. 4. Effect of two layers of water on the z -dependent density of the asymmetric M-point surface states of $\text{H}/\text{Si}(111)1\times 1$. The solid curve refers to two layers of VV-water, and the dot-dashed curve to a bottom layer of VV-water and a top layer of SR-water. Positions of the planes of silicon, capping hydrogen, and water oxygens are indicated by labeled vertical lines beneath the axis.

FIG. 5. The effect on the z -dependent density of the M-point surface states of $\text{H}/\text{Si}(111)1\times 1$ produced by one layer of water in energetically unfavorable sites. The solid curve refers to the bare surface result, the dot-dashed curve to a layer of SR-water, and the dashed curve to a layer of VV-water. Positions of the planes of silicon, capping hydrogen, and water oxygens are indicated by labeled vertical lines beneath the axis.

FIG. 6. The effect on the z -dependent density of a Γ -point valence band of H/Si(111)1 \times 1 produced by one layer of water in energetically unfavorable sites. (a) The solid curve refers to the bare surface result, and the dot-dashed curve to a layer of SR-water. (b) The solid curve refers to the bare surface result, and the dashed curve to a layer of VV-water. Positions of the planes of silicon, capping hydrogen, and water oxygens are indicated by labeled vertical lines beneath the axis.

Fig 1

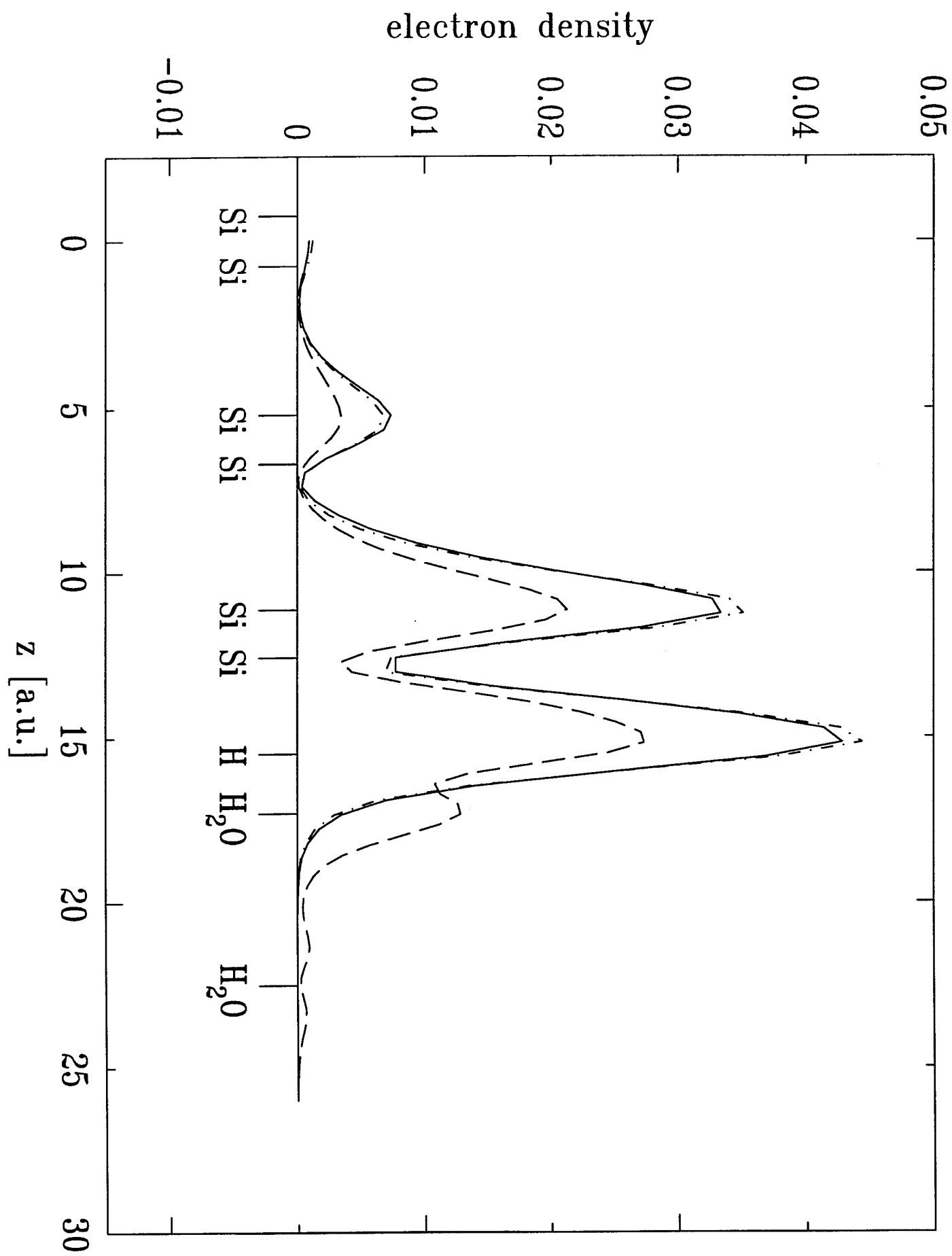


Fig 2

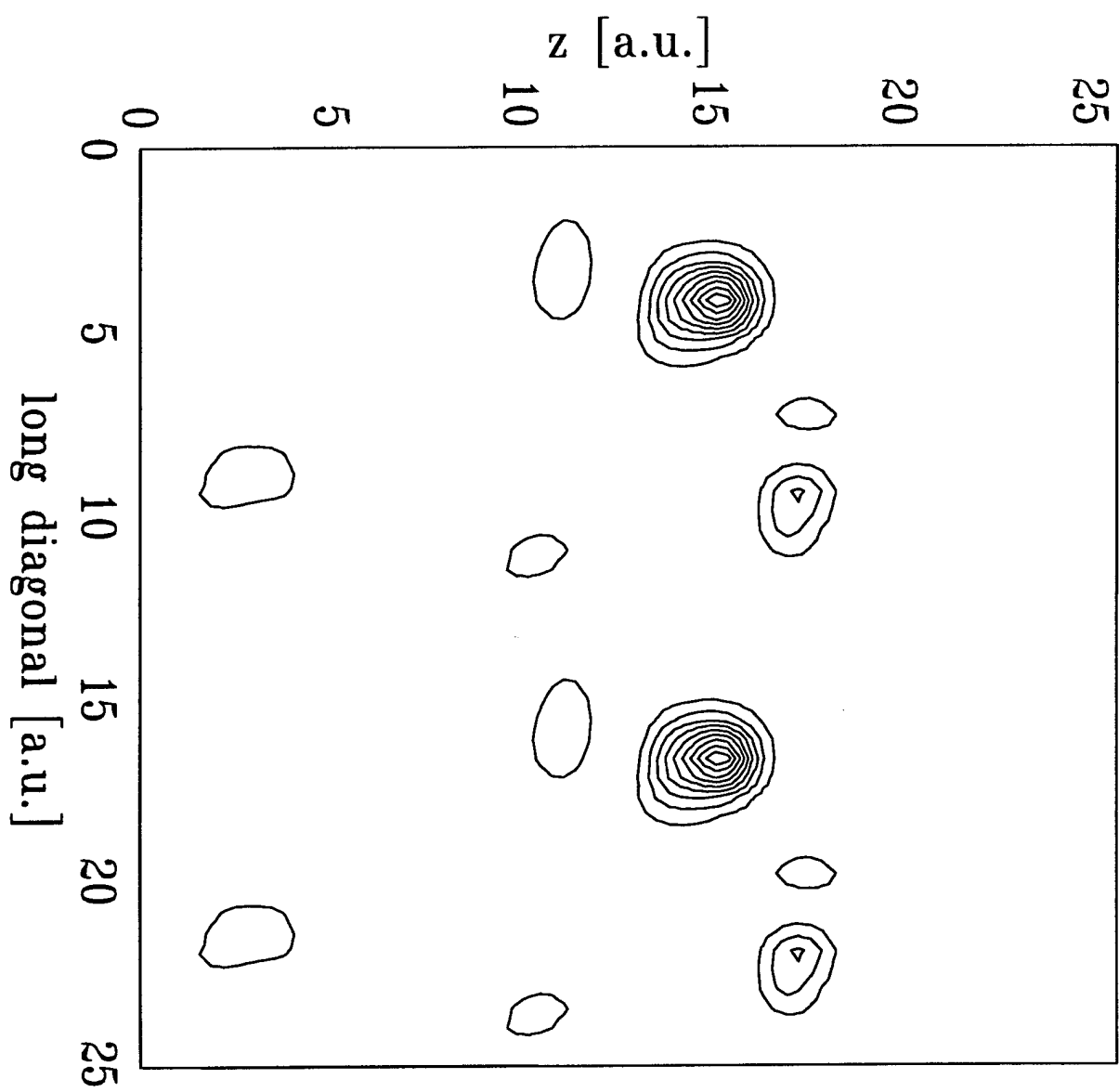


Fig 3a

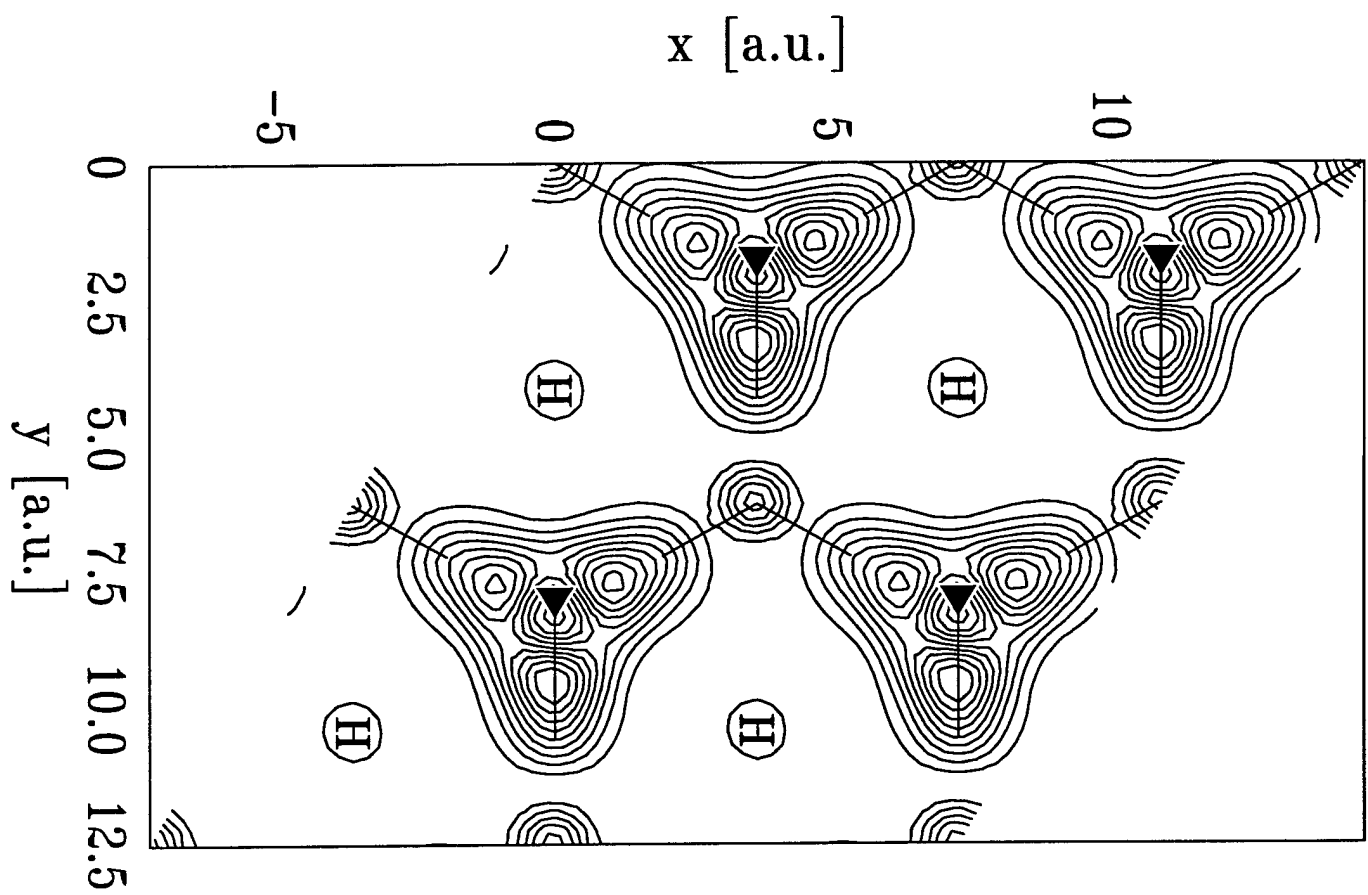


Fig 3b

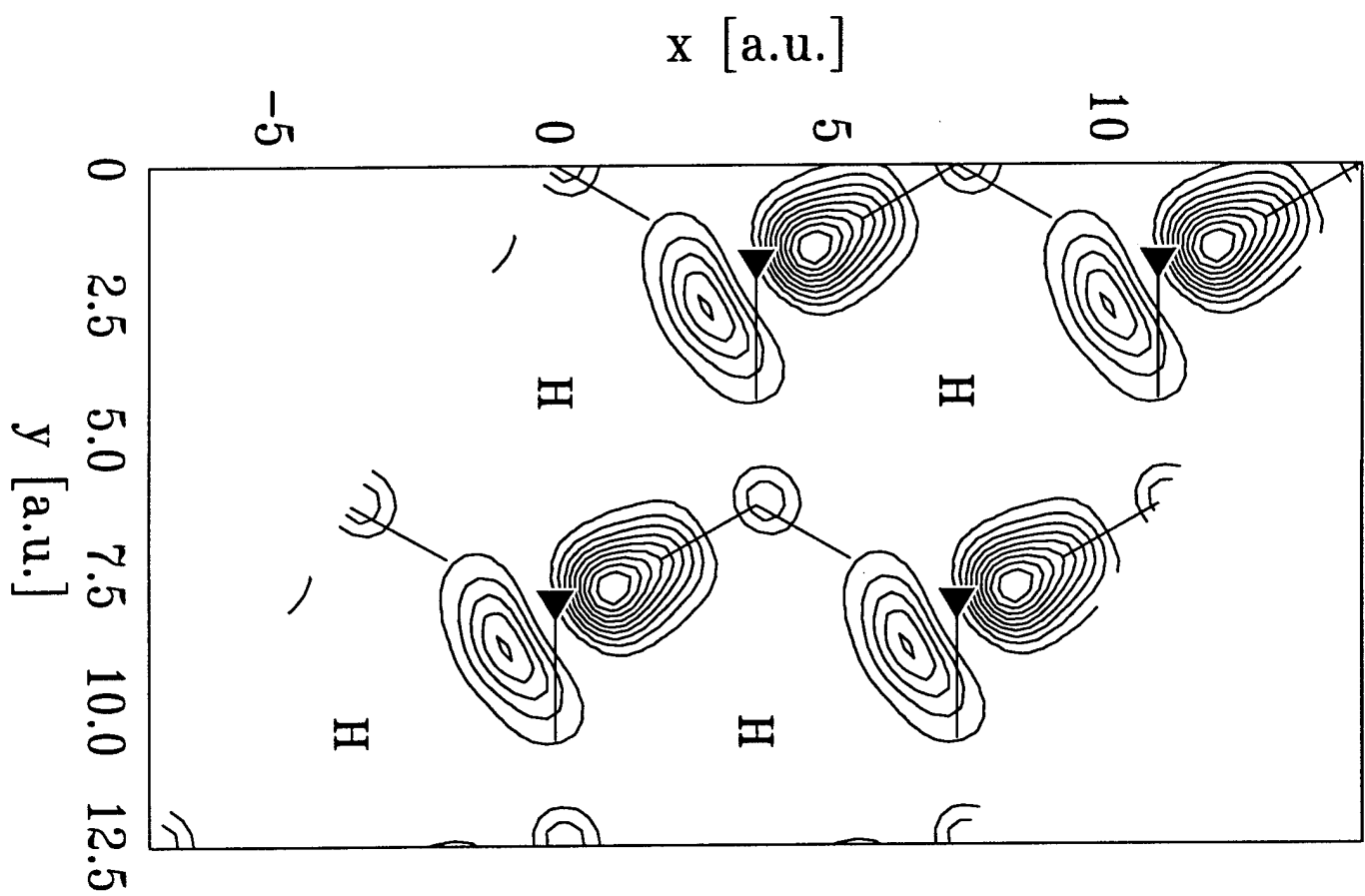


Fig 4

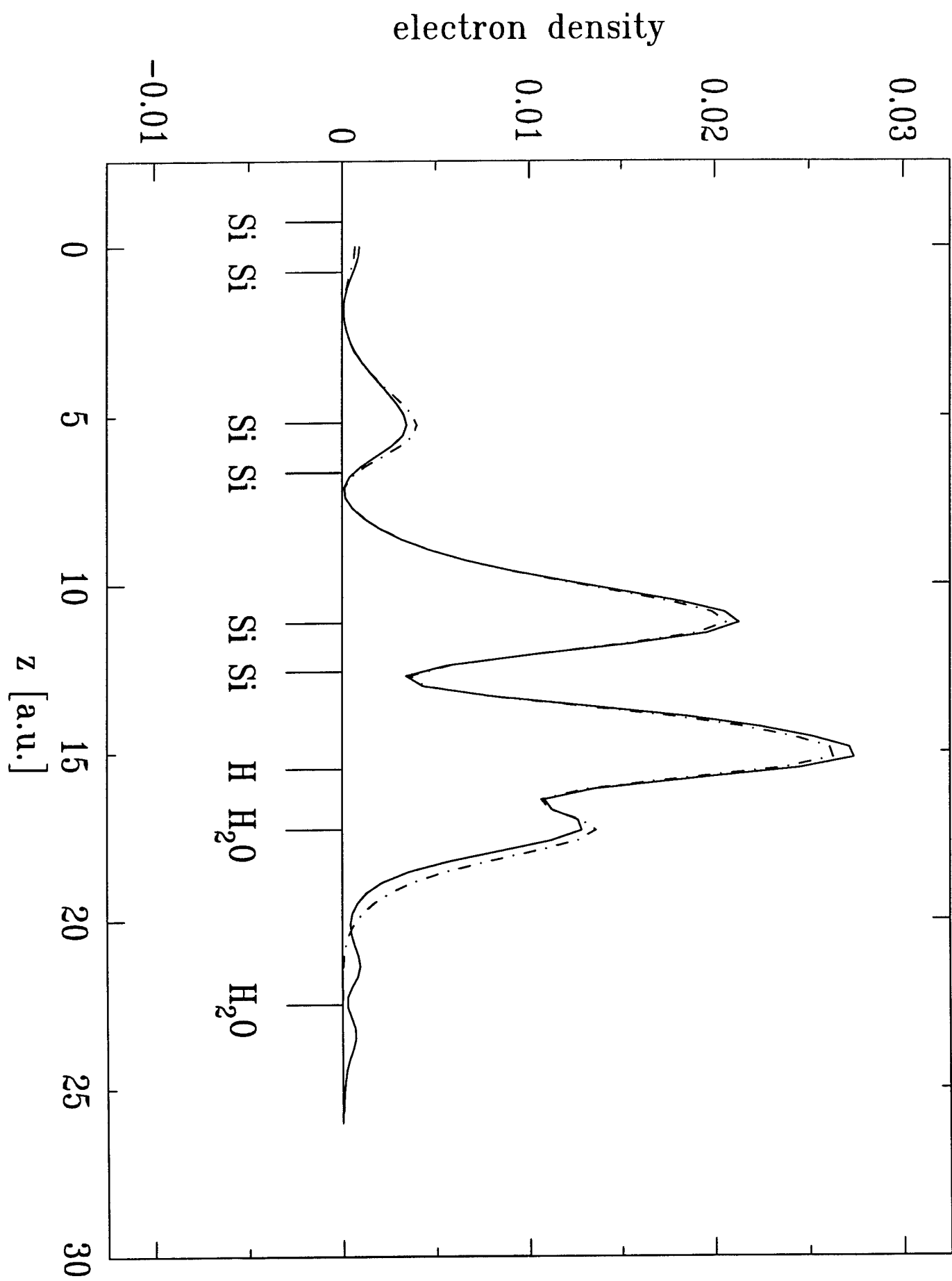


Fig 5

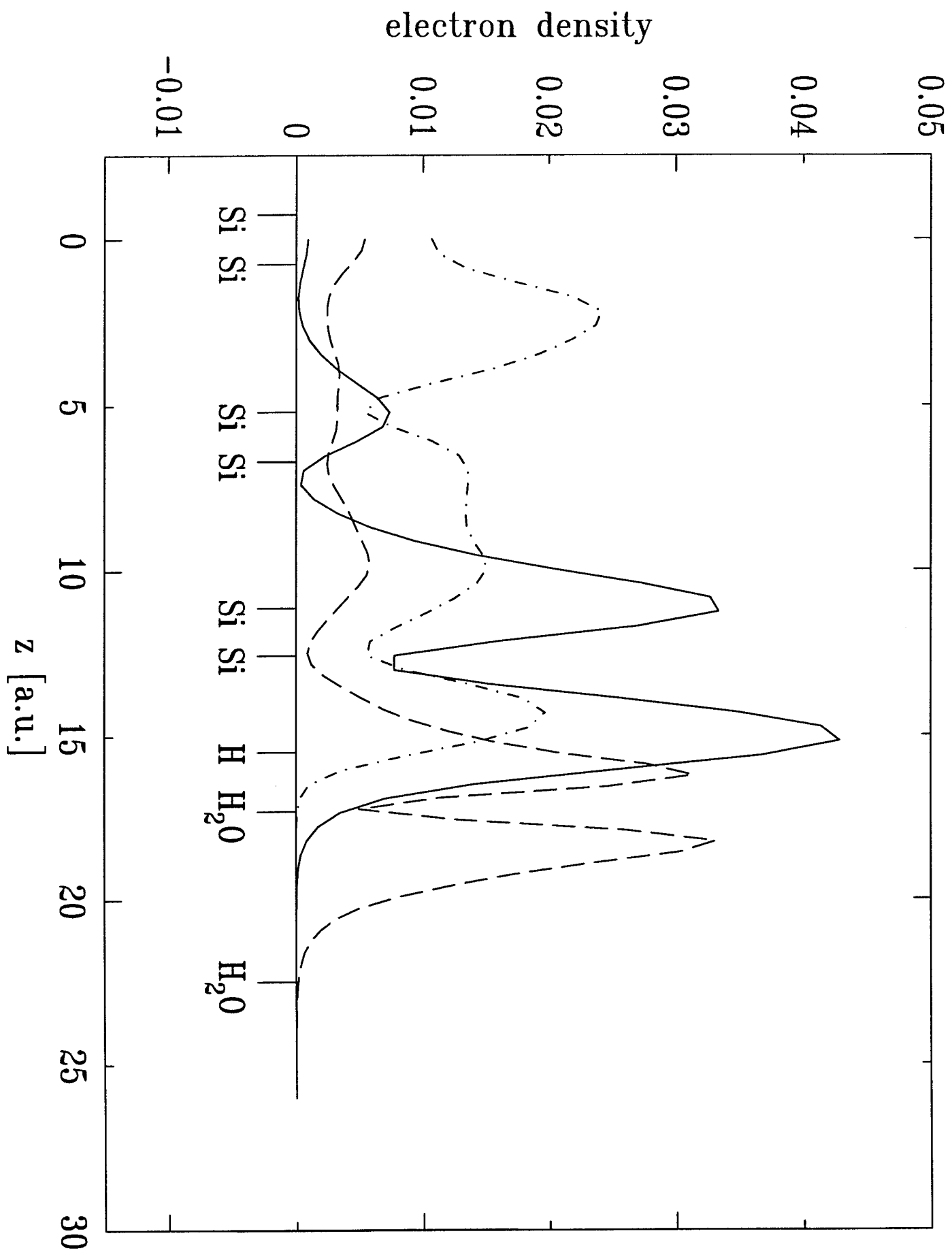


Fig 6a

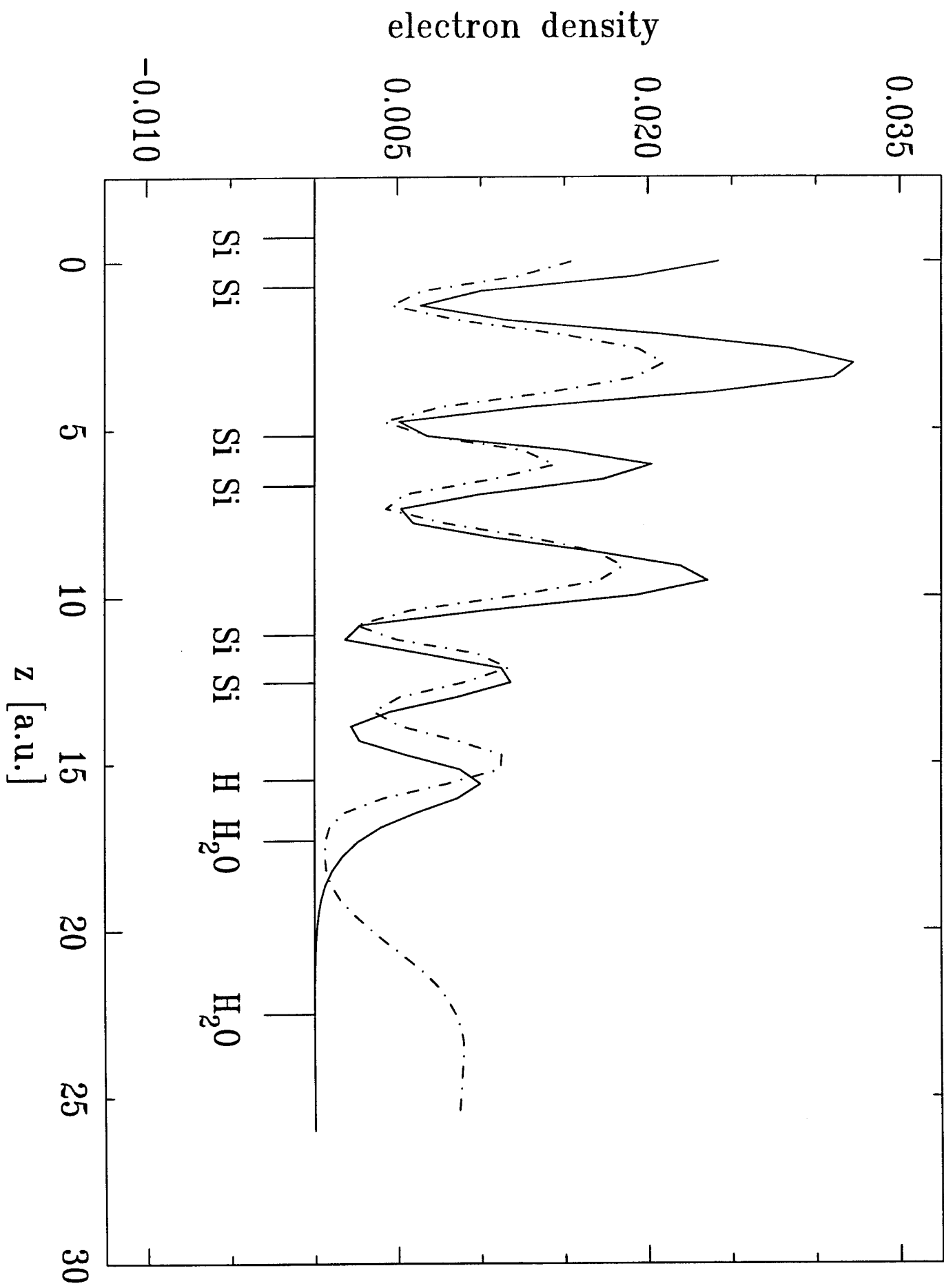


Fig 6b

